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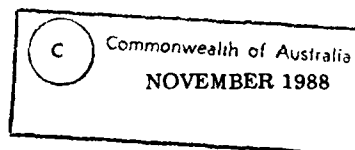
CATHODIC PROTECTION : A COMPARISON OF RESULTS OF LONG- AND
SHORT-TERM TESTING OF ALUMINIUM SACRIFICIAL ANODES

J.J. Batten, B.T. Moore
and B.S. Smith

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ABSTRACT

Work is presented which indicates that there can be serious discrepancies between measurements of the efficiency of aluminium galvanic (sacrificial) anodes when the results of long- and short-term testing procedures are compared. In some cases the correlation between the results obtained by the above two test methods can be very poor. These results cast serious doubts on the value of the short-term test carried out to the specification AS 2239-1979 for estimating the efficiency of these anodes.



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CATHODIC PROTECTION : A COMPARISON OF RESULTS OF LONG- AND SHORT-TERM TESTING OF ALUMINIUM SACRIFICIAL ANODES

1. INTRODUCTION

Cathodic protection is one of the most important anti-corrosion systems used by the Royal Australian Navy (RAN) to reduce the ravages of sea water corrosion of the hulls of their ships. This system is applied by one of two methods, viz. impressed current or galvanic (sacrificial) anodes. The choice and detailed design of a satisfactory cathodic protection system requires selection of the most suitable materials, and each system contains inherent advantages and disadvantages. Although cathodic protection usually works extremely well on hull areas continuously immersed in the sea, there are still problems that require elucidation: for example, passivation of some sacrificial anodes.

For the galvanic (sacrificial) system, the RAN has standardized on the use of hull anodes based on aluminium [1]. Most of these aluminium anode alloys are based on a ternary composition of the type Al-Activator-Zinc [2,3,4], where the activator is usually mercury, indium, gallium or tin and is used in low concentrations (e.g. 0.02-0.05%). Zinc is normally present in concentrations of 2-5% and acts as a secondary activator. In conjunction these activators upset the integrity of the naturally forming passive oxide which normally protects aluminium.

Although aluminium anodes are used extensively, experience has shown that they are sensitive to passivation and are affected by impurities [4,5]. These impurities may cause galvanic corrosion on the anode surface (i.e. loss of metal without production of externally useful current) and this will reduce anode efficiency. Similarly, intergranular attack resulting in loss of grains or larger metallic particles will also cause a reduction of anode efficiency. It is important, therefore, that dissolution be uniform over the anode surface. Uneven dissolution may also lead to increased underwater noise of naval ships.

For the RAN, it is desirable that satisfactory locally-produced commercial anodes be available with similar formulation to overseas anodes. These are made using

→ Contd

local raw materials and, therefore, may contain different impurity levels from those produced overseas.

It is necessary, therefore, that an evaluation be made of commercially produced anodes that may be used for the cathodic protection of Australian Naval vessels. This evaluation can be done either using short-term accelerated testing procedures or by long-term (i.e. 12 months or more) field trials. One such short-term test that has been used [6,7] to assess the performance of aluminium galvanic anodes is based on the Australian standard specification AS 2239-1979, Appendix C ~~10~~.

The purpose of this paper is to give some indication of the reliability of the short-term test in AS 2239 to predict the long-term efficiency of aluminium alloy galvanic anodes for use in cathodic protection systems in sea water. (R.C.)

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

The chemical composition limits for the aluminium alloy anodes are listed in Table 1 [8]. The alloys contain 2 to 5% zinc and 0.01 to 0.05% indium together with small amounts of other elements. Commercially-produced anodes, to the above chemical specification, were used in the field trials without any further treatment. The anodes were individually mounted on PVC backing boards. Each anode contained a cast-in steel strap which was used to suspend the anode and also to supply the electrical connection.

Two separate tests were conducted. In 1979 anodes of Types A1 and A2 were tested, while in 198~ the test programme was expanded to also include anodes of Type A4. Because these anodes were obtained at different times it is unlikely that any two anodes of one type would be from the same batch. However, all conformed to the composition of their respective types in AS 2239 [8].

A sample was cut from the end of each anode, and some of this was used in the short-term tests. The cut surfaces and edges of these were smoothed using a finisher. These samples were degreased and pickled in concentrated nitric acid before being washed, dried and weighed. For one of the short-term tests (see later) the amount of surface in the cast condition that was exposed to the sea water was varied.

After the test period, the field-trial anodes were scrubbed in hot water, dried and weighed. The specimens from the short-term test were rinsed in hot running water, pickled for ten minutes in concentrated nitric acid, washed with distilled water and ethanol, dried with hot air and weighed. Metal losses which occurred during both tests were recorded.

2.2 Anode Test Facility for the Field Trial

2.2.1 Field Trial, 1979

A floating dock at Williamstown, Melbourne, Australia, was used in this trial as the steel cathode [9]. It was moored in a relatively sheltered area where the water temperature ranged from about 13° to 18°C. The anodes were freely suspended at a distance of about 2 m from the side of the floating dock (see Fig. 1). Copper cable with a resistance of 0.0011 ohm/m was used to connect each anode to a common busbar via individual 0.0100 ± 0.0002 ohm standard resistors. Current from each anode could then be determined at any time by measuring the potential drop across its own resistor. A multi-point chart recorder was used to record these currents at hourly intervals throughout the test period of 308 days. To simulate ship-mounted operation of the anodes, the hull potential of the dock (measured at the busbar) was maintained constant at -820 mV to a Ag/AgCl reference electrode for the duration of the experiment.

2.2.2 Field Trial, 1987

The floating dock was unavailable for this trial so a new anode test facility was constructed from two large steel sections (Figs. 2 & 3), consisting of pieces of scrap steel welded together and submerged to a depth of about 10 m on the open-water side of Breakwater Pier (Fig. 4), Melbourne. Once submerged, the above two sections were connected to form the new cathode.

The test procedure used at this new site was similar to that used in the previous test. The anodes were hung in 10 m deep water on the calm-water side of Breakwater Pier (Fig. 5) at a depth of about 5 m. Currents were recorded for several minutes at four specific times per day throughout the test.

2.3 Laboratory Test Procedure

These tests were conducted in accordance with Appendix C of Australian Standard AS 2239-1979. In this constant current test, the anode current density is maintained between 0.5 mA/cm^2 and 0.7 mA/cm^2 in a non-metallic tank containing a stirrer and an aluminium cathode. The prescribed minimum test period is 10 days, and during this time the sea water is changed when 0.1 A.h has passed for each 1 litre of sea water in the cell. The test is conducted at ambient temperature.

Electrical connection was made to the test-specimen by means of a threaded brass rod which was isolated from the sea water by a leak-proof assembly consisting of a glass tube and a PTFE gasket (similar to the mount used in ASTM G5).

3. RESULTS AND DISCUSSION

Results are presented in Tables 2 and 3. For the 1979 field trial the mass loss figures in Table 2 show that the rate of metal loss from anodes A1 and A2 are similar. The Faradaic efficiency (89%) of the Al-Zn-In-Cd alloy anodes (A1) and their current output characteristics were very satisfactory. On the other hand, the Al-Zn-In-Mg alloy anodes (A2) performed relatively poorly with respect to both efficiency (61%) and current outputs.

For the corresponding short-term experiments (Table 3) the average efficiencies of anodes A1 and A2 are about 87% and 81% respectively. The correlations between the efficiencies obtained by the two evaluation methods are presented in Table 4, from which it is clear that the correlation for A2 anodes is poor. This suggests that for A2 anodes there is some difference in dissolution behaviour between the long- and short-term tests. It was because this poor correlation cast doubt on the validity of a testing procedure specified in an Australian Standard that it was decided to repeat the work (the 1987 trial) at the new anode test site at Breakwater Pier.

The results of the 1987 trial, which also included A4 anodes, are presented in Tables 2 and 3. Table 4 indicates that the correlation between the efficiencies obtained by the two evaluation methods is again poor for A2 anodes - in fact worse than the correlation obtained previously. For A1 anodes correlation was again good, although efficiencies were lower than in 1979 (possibly due to a difference between batches of anodes). A4 anodes showed fair correlation, the long-term test giving higher efficiencies than the short-term test in this instance.

The appearance of anodes after the long-term trial is shown in Figures 6 and 7. The Al-Zn-In-Cd alloy anode (A1) surfaces were generally quite rough (see Figs. 6 & 7) with grooves 5 to 8 mm deep. The Al-Zn-In-Mg alloy anodes (A2) and the Al-Zn-In alloy anodes (A4) were more uniformly corroded (Figs. 6 & 7), although the micro-roughness on all was appreciable. Quantities of fine metallic particles were separated from the bulky corrosion products of all anodes, indicating a significant contribution to poor efficiency by direct metal loss due to undercutting of dendritic remnants and/or grain boundary attack. These effects were also observed in many of the short-term tests.

The anode test procedure outlined in AS 2239 can be regarded as an accelerated corrosion test, and it is well appreciated that there are many pitfalls associated with this practice of predicting long-term corrosion behaviour. Because these tests need to be carried out at extremes of stimuli, the corrosion environment is not representative of that pertaining to the long-term test.

Thus, for example, in this short-term test the accumulation of corrosion products in the reaction cell could influence the corrosion mechanism (e.g. by autocatalysis) and thereby induce a new corrosion process that would not occur in an environment that was continuously changing [10, 11], e.g. in the open sea. Such false corrosion mechanisms could result in misleading assessments.

Further, in a short-term test often the extent of corrosion is small, and thus the resulting efficiency could mainly depend on the surface properties of the sample under test (e.g. different crystal size to the bulk of the sample, the bulk material may have a more uniform microstructure or a slightly different chemical composition, or

some parts of the surface may be passive). Alternatively, in a long-term test, the result will largely depend on the bulk properties of the sample.

In spite of the above, in our short-term test procedure not only was the cast surface exposed to the environment but so also were the cut surfaces (see Table 3). Thus it would be expected that surface imperfections and impurities arising from the casting process would have less influence. We conclude from our results, therefore, that the lack of correlation we have observed is not dominated by the surface created by the casting process.

Although a good correlation between the results of the two test methods was obtained in two out of the three anode types tested, the one poor correlation does cast doubt on the reliability of using this short-term test procedure to predict the long-term behaviour of anodes. It would appear that, while an alloy which fails this short-term test may reasonably be rejected, one which passes will need to undergo a long-term test for confirmation of its acceptability.

The present work has indicated that the anodes with poor long-term performance gave poor correlation. A study of the reasons for this poor efficiency may give an indication of the way to develop a more reliable short-term test. This will be the topic for future study.

4. CONCLUSION

It is concluded from our results that the short-term test for determining the efficiency of aluminium galvanic (sacrificial) anodes for cathodic protection, as defined in Appendix C of Australian Standard AS 2239-1979, is not reliable.

5. ACKNOWLEDGEMENT

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TABLE 1

Requirements for Chemical Composition Limits of
Aluminium Alloy Anodes

Element	Chemical Composition, Percentage*		
	Designation A1	Designation A2	Designation A4
Zinc	2.1-2.7	3.0-5.0	2.8-3.5
Indium	0.017-0.025	0.02-0.05	0.01-0.02
Cadmium	0.008-0.012	-	-
Silicon	0.05-0.10	0.05-0.20	0.11-0.21
Iron	0.15 max.	0.05-0.15	0.10 max.
Magnesium	-	0.6-2.2	-
Titanium	-	0.02-0.05	-
Copper	-	0.01 max.	0.006 max.
Mercury	-	-	-
Other impurities	0.01 each max.	0.02 each max. 0.05 total max.	0.02 each max.
Aluminium	Remainder	Remainder	Remainder

* Taken from AS 2239 [8]

TABLE 2

Results for the Field Trials Conducted on Aluminium
Anodes for Cathodic Protection

Designation of Anode	Date of Trial	Specimen Code	Duration of Trial (days)	Total Current Flow (A.h)	Actual Mass Loss (g)	Alloy Consumption Rate (kg/A.year)	Anode Efficiency (%)	Average Efficiency (%)
A 1	1979	1	308	4490	1706	3.33	90	89
		2	308	3861	1502	3.41	88	
		3	308	4462	1702	3.34	90	
	1987	4	376	2394	1127	4.12	73	77
		5	376	3220	1330	3.62	83	
		6	376	2819	1267	3.94	76	
A 2	1979	1	308	3054	1769	5.07	60	61
		2	308	3006	1611	4.69	65	
		3	308	2730	1662	5.33	57	
	1987	5	376	1744	1786	8.97	34	48
		6	376	1733	1690	8.54	36	
		7	376	2854	1360	4.17	73	
A 4	1987	1	370	3341	1330	3.49	86	86
		2	370	3445	1340	3.41	88	
		3	370	3180	1280	3.53	85	

TABLE 3

Results for the Short-Term Tests Conducted on Aluminium
Anodes for Cathodic Protection

Designation of Anode	Date of Trial	Specimen Code	Duration of Test (h)	Current Density (mA.cm ⁻²)	Weight Loss (g)	Consumption Rate (kg/A.year)	Anode Efficiency (%)	Average Efficiency (%)	Percentage Surface Area in Cast Condition
A1	1979	1	336	0.93	1.581	3.44	87	87	
		2(a)	336	0.68	1.585	3.45	87		
		3(a)	336	0.69	1.578	3.43	88		
		4(a)	336	0.67	1.604	3.49	86		
		2(b)	406	0.68	1.920	3.45	87		
		3(b)	406	0.67	1.897	3.41	88		
	1987	4(b)	312	0.59	3.181	4.13	73	77	50
		4(c)	309	0.62	1.761	3.84	79		60
		5(a)	310	0.61	1.816	3.67	82		60
		5(b)	308	0.60	2.264	4.03	75		30
		6(a)	308	0.59	2.165	3.85	78		25
		6(b)	312	0.70	3.118	4.05	75		60
A2	1979	1(a)	307	0.72	1.424	3.68	82	81	
		2	307	0.68	1.474	3.81	79		
		3	307	0.68	1.440	3.73	81		
		4(a)	307	0.67	1.440	3.73	81		
		1(b)	406	0.97	2.117	3.81	79		
		4(b)	406	0.68	2.070	3.72	81		
	1987	5(a)	312	0.61	1.806	3.70	81	79	40
		5(b)	309	0.58	1.896	4.13	73		20
		6(a)	308	0.70	2.287	4.07	74		40
		6(b)	310	0.57	1.740	3.51	86		20
		7(a)	312	0.60	1.739	3.56	86		40
		7(b)	309	0.60	1.876	4.09	74		20
A4	1987	1(a)	334	0.53	2.251	3.69	82	79	40
		1(b)	329	0.55	2.370	3.94	77		20
		2(a)	329	0.68	2.395	3.99	76		30
		2(b)	334	0.64	2.192	3.59	84		10
		3(a)	334	0.52	2.249	3.69	82		10
		3(b)	329	0.58	2.441	4.06	74		30

TABLE 4

Correlation between the Results for the Efficiency of Anodes
Obtained by Long-Term and Short-Term Testing

Year of Test	Correlation for each Anode*		
	%		
	A1	A2	A4
1979	100	75	-
1987	100	61	110

* Defined as $\frac{\text{Efficiency of long-term test}}{\text{Efficiency of short-term test}} \times 100$

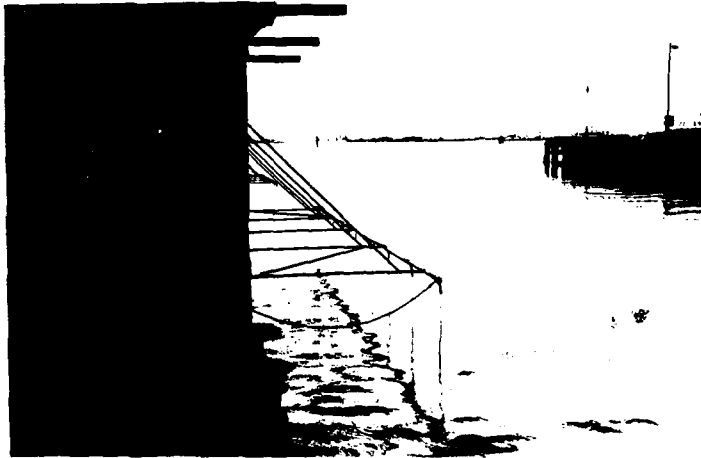


FIG. 1 (upper) Racks on the side wall of the floating dock.

FIG. 2 (lower) Floating crane used to transfer the two large steel sections to Breakwater Pier.

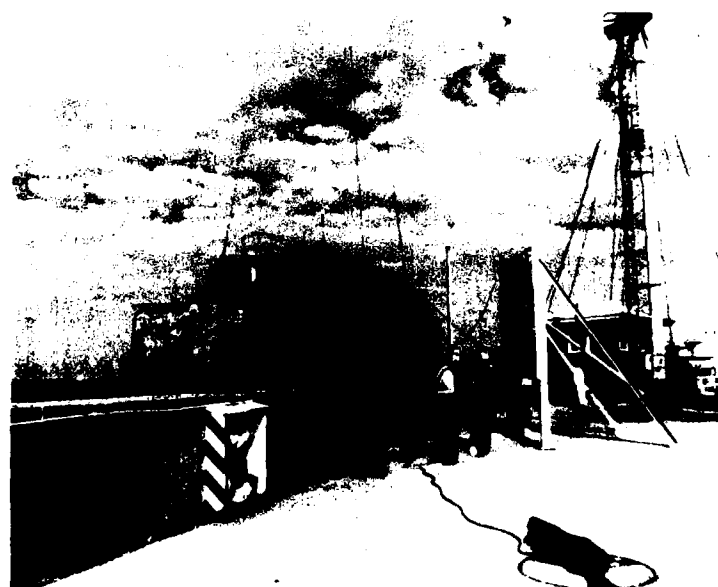
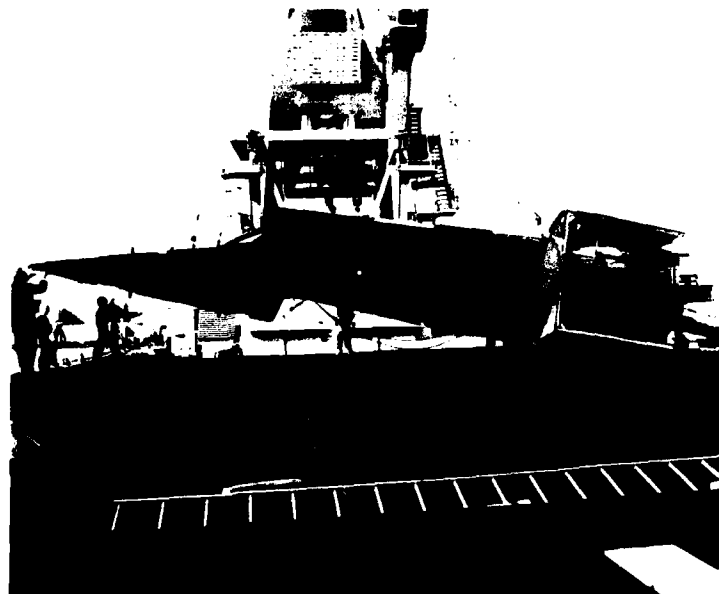


FIG. 3 Two large steel sections used to form the anode test site at Breakwater Pier.



FIG. 4 (upper) Steel section being submerged.

FIG. 5 (lower) Calm-water side of Breakwater Pier where the anodes were hung.

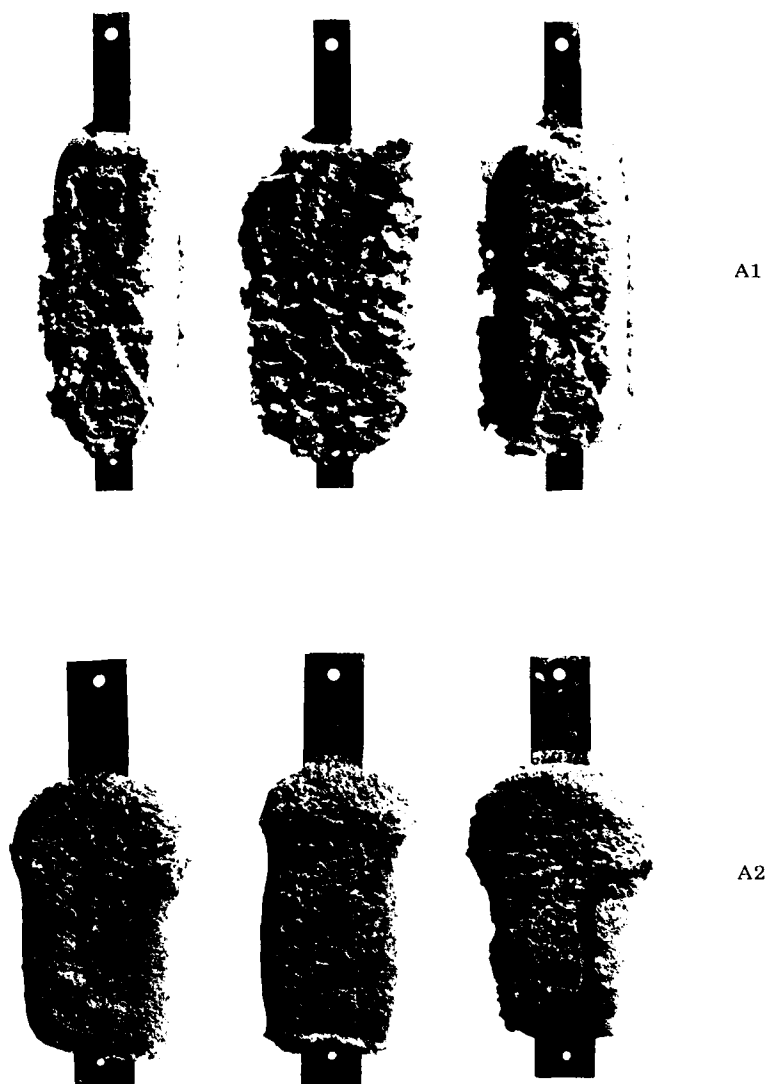


FIG. 6 Appearance of the anodes A1 and A2 at the end of the 1979 field trial and after being cleaned.

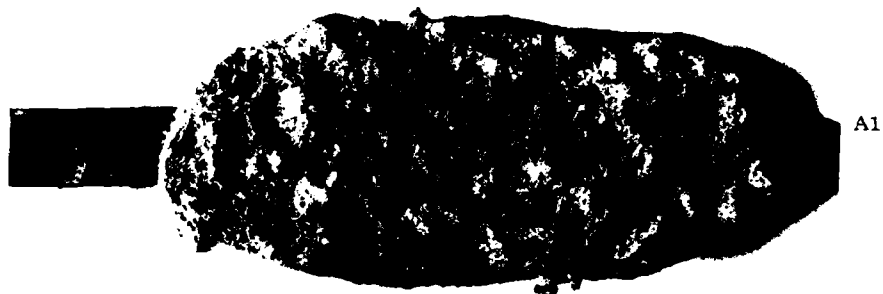


FIG. 7 Appearance of the anodes A1, A2 and A4 at the end of the 1987 field trial and after being cleaned.

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